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Phosphonated graft copolyimide for direct methanol fuel cell

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Introduction

Direct methanol fuel cells (DMFCs) is promising energy source for portable power applications[1]. The two major disadvantages of DMFCs applications; the low activity of methanol electro-oxidation catalysts and methanol crossover through polymer electrolyte membranes, inhibit commercialization. The present polymer electrolyte membrane used in DMFCs such as Nafion has large methanol crossover from the anode to cathode.[2] It leads to secondary reaction, mixed potential of oxidation and reduction at electrode, decreasing energy and power density, and reducing overall performance. Many researches reported that perfluorosulfonated membranes with clear ionic channel have high methanol crossover and are not suitable for applications with a methanol feed concentration higher than 10 wt.%.[3]

Several phosphonic acid-containing polymers have been studied and their synthetic route were proposed in 2 different pathways; post-phosphonation of polymer and polymerization of phosphonic acid-containing monomer.[4-6] For example the introduction of phosphonic acid group to pre-made fluorinated polymer backbone is studied and some groups synthesized new phosphonic acid containing fluorinated monomer which able to copolymerize with other fluorinated polymers. These phosphonic acid containing membrane has poor conductivities due to low phosphonation level.[7-8] Aromatic polyimides are widely studied in fuel cell application due to their high thermal stability and mechanical strength.[9-13] Many types of sulfonated polyimide membranes have been developed for fuel cell including DMFCs. For instance, the sulfonated naphthalenic polyimide has recently reported for DMFCs application. The Yuming et al prepared the sulfonated polyimide membrane via one step polymerization and their obtained membrane displayed desirable proton conductivity ranged from 7.9×10^{-3} to 7.2×10^{-2} s/cm and low methanol permeability of less than 2.85×10^{-7} cm^2/s.[1]

Only few researches have focused on phosphonated polyimide. Taking advantages of high thermal properties and mechanical strength of polyimide, in combination with the capability to form strong hydrogen bond and thermal stabilities of phosphonic acid we come up with the novel phosphonate grafted copolyimide. The new synthesis route and studied the phosphonate branched copolyimide which derived from NTDA, 4,4'-Oxydianiline (ODA) and 3,3'-diaminobenzidine was studied. The membrane displayed comparable proton conductivity in PEMFCs. In this work, the methanol permeation and proton conduction properties of these phosphonate graft polyimide membranes were investigated and compared with those of Nafion 117 to evaluate the potential for DMFC application.

Results and discussion

The PBPI was comprised of hydrophobic and hydrophilic blocks. The block branches were easily controlled, since the two blocks, PI-A and paPI-C, were separately synthesized and then reacted together to form the branched copolyimide namely PBPI as shown in Figure 1. The grafting step was confirmed by the disappearance of the –NH2 resonance at 6.55 ppm in phosphonated polyimide namely PEPI-C (Figure 2)

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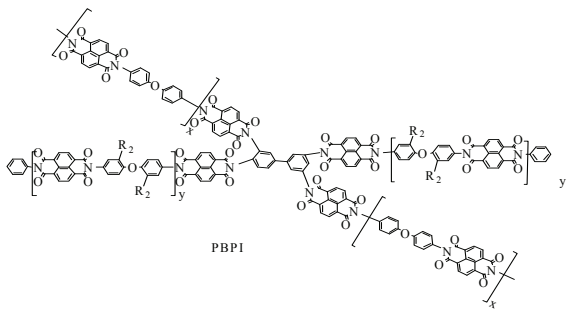

Figure 1 The phosphonate branched copolyimide structure

The phosphonation was confirmed by FTIR, specifically absorbances at 1235, 1190 and 930 cm^{-1} due to R(HO)2P=O stretching vibrations. All membranes were prepared by blending with 20% of polyimide (PI-A) solution in m-cresol. A comparison of IEC values of phosphonate polyimide and grafted copolyimide powder and their membranes are shown in Table 1. The IEC of all phosphonate graft polyimide membranes (fPBPI-1, fPBPI-2 and fPBPI-3) decreases due to the dilution of the phosphonic acid by blending the unphosphonate polyimide, PI-A.

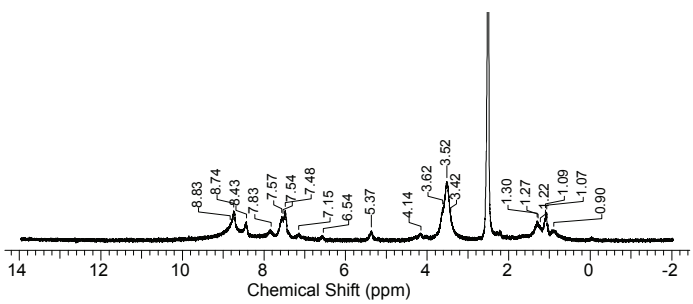

Figure 2 The example of ^{1}H-NMR spectra of phosphonate ester derivative of polyimide, PEPI (DP=32%), in DMSO-d_6

Table 1. The IEC of phosphonate polyimides and grafted copolyimide samples

Polymer	Degree of phosphonation	IEC_{nmr} (meq/g)	$IEC_{titration}$ (meq/g)
PI-A	-	-	-
paPI-C1	30%	1.48	1.45
paPI-C2	42%	2.10	1.98
paPI-C3	55%	2.72	2.68
PBPI-1	-	-	1.02
PBPI-2	-	-	1.38
PBPI-3	-	-	1.67
fPBPI-1*	-	-	0.92

Nafion®117	-	-	0.91

*All membrane were prepared by blending with 20% PI-A in m-cresol

All membranes have low water uptake due to the addition of hydrophobic non-phosphonate part and was agreed with swelling results as shown in Figure 3. As expected properties, the membrane, fPBPI-3, with highest IEC~1.43 meq/g, obtained from highest phosphonation level of paPI-C3, shows highest swelling ratio at 16% and water uptake at 24%. Comparing to Nafion®117 with 18% swelling and 32% water uptake, the fPBPI-3 shows lower water uptake and swelling while its IEC value is higher. This can be explained by the difference in microstructure, Nafion®117 has extremely high hydrophilicity of sulfonic acid group[1] while the PBPI membrane has high hydrophobicity.

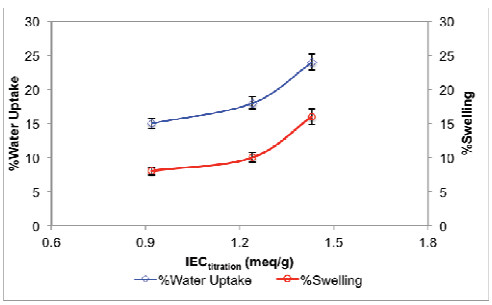

Figure 3 The water uptake and swelling property of phosphonate graft copolyimide membrane (fPBPI-1, fPBPI-2 and fPBPI-3)

A comparison of the thermal stability of PI-A, paPI-C and PBPI system is shown in Figure 4. All of the polymers were stable to at least 400°C, because of the excellent stability of the imide groups. PI-A was stable to ~550°C, where degradation of the imide groups occurred. The paPI-C was less stable, probably as a result of the phosphonic acid groups. The phosphonated polymers also had a small mass loss below 100°C, which was most likely water. Comparing among paPI-C system, as the degree of phosphonation increased, the weight losses around 475°C increase and the degradation temperature doesn't decrease significantly. This observation agrees with in PBPI system. From Table 2, the methanol permeability of obtained PBPI membranes increase from 8.3×10^{-8} to 4.4×10^{-7} cm^2/s with increase of phosphonation level. It's noticed that the IECs of PBPI films are close to Nafion®117 but the PBPI film shows lower methanol permeability by a magnitude.

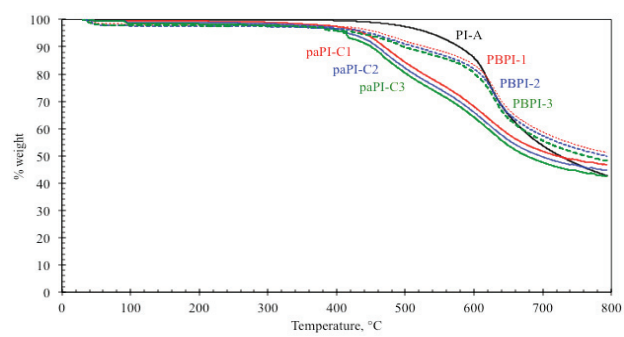

Figure 4 Thermal properties of all polyimide samples

Table 2 The methanol permeability and proton conductivity

Sample	Methanol permeability (cm^2/s)	Proton conductivity (S/cm)
fPBPI-1*	8.3×10^{-8}(4%)	3.42×10^{-3}(4%)
fPBPI-2*	2.6×10^{-7}(12%)	1.08×10^{-2}(13%)
fPBPI-3*	4.4×10^{-7}(21%)	2.42×10^{-2}(30%)
Nafion®117	2.1×10^{-6}(100%)	8.2×10^{-2}(100%)

* All membrane were prepared by blending with 20% PI-A in m-cresol

* All membrane were prepared by blending with 20% PI-A in m-cresol

This reduction of methanol permeability is due to the amount of hydrophobic part is added during the membrane preparation and the difference in microstructure between these two polymers as mentioned before. However the Nafion®117 membrane displays the three times higher proton conductivity that compared to fPBPI-3, regardless to five times higher methanol permeability than fPBPI-3. The proton conductivity of PBPI membranes at room temperature and hydrated condition are investigated. With increasing of phosphonation level, proton conductivity of PBPI increases and reaches the maximum at 2.42×10^{-7} s/cm. The fPBPI-3 with highest phosphonation level in this study displays about one-third lower than Nafion®117 in spite of much higher IEC value. It seems that the main reason for lower proton conductivity is due to lower water uptake. In addition it might cause from the different of size and distance between ionic clusters. Moreover the proton conductivity of phosphonate grafted copolyimide is slightly lower than sulfonated polyimide membrane which reported by many researchers[12,14] while the phosphonic acids are less acidic than sulfonic acids. It interestingly noted that the graft structure of phosphonated polyimide may compensate its disadvantage in low acidic of phosphonic acid and the bulky branched structure may form more hydrophobic/hydrophilic micro-phase separation and provide a wider transport channel than normal sulfonated polyimide.[15,16]

Conclusions

A new series of novel phosphonated branched-block copolyimide was synthesized using a combination of polycondensation and lithiation reactions and a tetra-amine coupling compound. The synthetic route was relatively simple and allows for facile adjustment of molecular weight of the backbone and side chains, as well as the phosphonation concentration. The phosphonated branched copolyimide was thermally stable to at least 450°C. The membranes display lower methanol crossover less than 4.4×10^{-7} cm^2/s and little lower proton conductivity comparable to Nafion®117.

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